Cobalt based emission control catalysts with high resistance towards halide poisoning

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ABSTRACT

Halide poisoning is a common problem in industrial exhaust control. In this study new catalysts have been searched, which effectively oxidize hydrocarbons in the presence of methyl bromide as halide containing pollutant. The search focused on low cost mixed metal oxides based on Ce, Co, Cr and Ni. Noble metals, Cu and Mn were neglected. High throughput technologies have been applied to accelerate the development process. Screening was based on emissivity corrected IR-thermography. Potential hits were validated using conventional gas phase flow catalysis. The tested catalysts were arranged in four ternary metal oxide composition spreads: Ce–Co–Cr, Ce–Co–Ni, Ce–Cr–Ni and Co–Cr–Ni. Out of the screening, Co–Ni mixed oxides had high CO conversion rates in the presence of methyl bromide. Further these catalysts were optimized by catalyst doping and composition variation. In a 50 h long term experiment the CO oxidation in the presence of methyl bromide was checked for our best catalyst $Ce_5Co_{90}Ni_5O_x$. Additionally, the effect of various metal oxide additives on catalytic performance and BET surface is described.

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1. Introduction

Exhaust control belongs to the important applications of heterogeneous catalysts. The main task of solid heterogeneous catalysts in exhaust control is the decomposition of hazardous air pollutants, such as CO, volatile hydrocarbons (VOCs) and halogenated VOCs, in complex gas mixtures into nontoxic carbon dioxide and water. In academic studies on catalytic oxidation of pollutants with different catalysts and variation of experimental conditions, often only one molecule is studied. These studies neglect the interplay between the gas molecules with each other and the competitive interaction between gas molecules and catalyst surface (competitive adsorption). Especially in the case of halogenated VOCs these competitive interactions of gas compounds and catalyst surface are instrumental for the catalytic activity. In a high throughput study on catalysts for exhaust gas cleaning with complex exhaust gas compositions it has been shown, that different catalysts qualify for different pollutants, which would imply selective catalyst developments for all individual pollutants [1]. In addition, pollutants compete among each other in surface interactions, which results in competitive deactivations for complex exhaust gas mixtures. Halogenated components in such exhaust gases create a special problem, since they deactivate many exhaust gas catalysts via surface halogenation. For example, the oxidation of CO with Pt–Pd catalysts in the presence

of 35 ppm methyl bromide (MeBr) requires temperatures of 320 °C while for noble metal free catalysts rapid deactivation is reported [2]. Exhaust gas containing CO and MeBr is produced for instance by terephthalic acid plants [3].

Several mechanisms for the catalyst deactivation during decomposition of halogenated VOCs have been discussed over the last decades [4–7]. Windawi and Zhang document the complex interaction between the gas components and the catalyst surface with a mixture of MeBr and toluene on two different supports (alumina and titania) with identical noble metal loadings [5]. For these experiments the light-off temperatures of the gas components depend on the interactions of the supports with MeBr. The important role of the support was confirmed by Toledo et al. in their study on the decomposition of chlorinated hydrocarbons with noble metals on different alumina supports [6]. Due to the broad range of performances on their alumina supports, they recommend zirconia or titania supports for decomposition of halogenated VOCs. Especially the catalytically active centres of metal oxide catalysts are affected under these conditions. Hopcalite, a Cu–Mn mixed-metal oxide catalyst, deactivates rapidly due to formation of copper and manganese halides [8]. This metal halide formation often results in loss of catalyst mass due to the volatility of many metal halides [9].

There is a need for more stable catalysts, which overcome the problem of deactivation. A promising and simple strategy is to stabilize catalysts of good initial activity by doping with other elements. Simple one at a time experimentation for such problems is too time consuming and costly. High throughput (HT) methods

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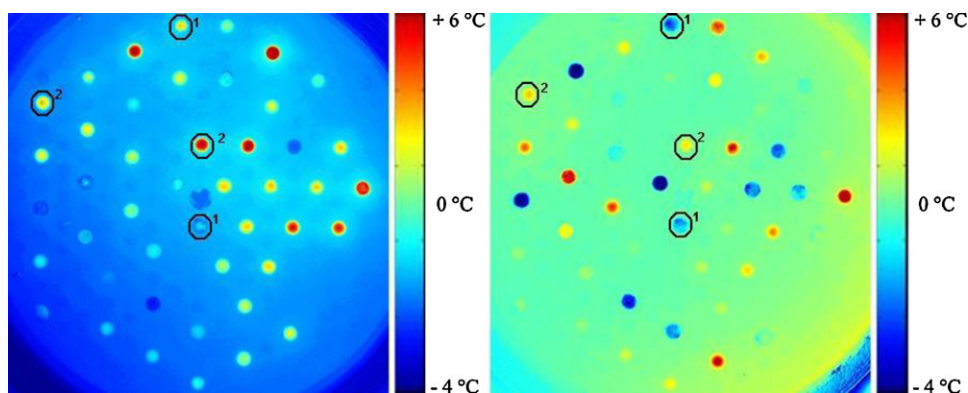 *E-mail address:* w.f.maier@mx.uni-saarland.de (W.F. Maier).

Fig. 1. EcIRT images: left: CO oxidation at 250 °C in the absence of MeBr, feed gas composition CO:O$_2$:N$_2$ = 3:10:87, flow 50 mL/min; right: CO oxidation at 250 °C in the presence of MeBr, feed gas composition MeBr:CO:O$_2$:N$_2$ = 1:3:10:86, flow 50 mL/min (1 = Ce$_5$Co$_{95}$O$_x$ (in Table 2 only the upper spot is considered); 2 = Ce$_{10}$Co$_{80}$Ni$_{10}$O$_x$).

combined with combinatorial chemistry are valuable screening tools for the discovering of materials under complex reaction conditions [10]. The advantages of HT methods are (1) low amount of material that is needed and (2) the investigation of many different material compositions in parallel under identical conditions. However, high throughput experimentation (HTE) can only be applied successfully, if a suitable screening technology can be applied. Combustion reactions, such as the combustion of hydrocarbons, are exothermic and the total oxidation of the pollutants is desired, which are ideal conditions for the application of IR thermography. Emissivity corrected IR thermography (ecIRT) is a valuable and very sensitive screening tool for exothermic reactions, which has been successfully applied to catalyst development and optimization in high throughput studies [11,12]. EcIRT is an optical screening system, which allows the parallel monitoring of the exothermicity of materials on a library. For example the heat of reactions of 206 catalysts on a library has been observed *in situ* [13]. Since IRT only identifies temperatures and by comparison changes of temperatures, the scientist conducting the experiment has to make sure, that temperature changes observed correlate with the desired heat of reaction. Erroneous results are produced not only, when exothermic or endothermic parallel reactions and sequential reactions take place, but also when the catalyst surface changes its emissivity due to reaction of the catalyst surface with feed gas components or when observed temperatures are outside the calibration range. This and other potential pitfalls have been described elsewhere [13,14]. In our ecIRT-experiments, up to 206 potential catalysts are placed in the wells of a slate library and the reagent gases flow over these materials. The heats of reactions, observed by the IRT camera position above the library, are the heat of the surface of the catalyst packings in the wells (see Fig. 1). Nothing is known about the heat of the catalyst bed itself. It should also be realized, that the reagents flow only over the catalyst bed, there is no flow through and little is known about the mass transport properties within the catalyst beds. Nevertheless, all catalysts on a library are tested under identical reaction conditions and relative performance can be used to select hits. Experience has shown, that false positives or negatives are common and validation of hits by conventional testing is required. Correlation of hits (ΔT of catalyst surface) from ecIRT with conventional results (conversion) is worthless due to the differences of the observant. Therefore, ecIRT is only used here to select hits, no correlation of these hits with conventional testing has been attempted.

Herein we report the results of our search for noble metal free catalysts to substitute Cu–Mn oxides (hopcalites) as combustion catalysts for halogen containing industrial exhaust gas cleaning. In

this study MeBr was used as model poison during the combined oxidation of CO and benzene.

2. Experimental

2.1. High throughput technology

2.1.1. High throughput syntheses of catalyst libraries

The catalyst libraries were designed by the in-house software "Plattenbau" [15]. Composition tolerant recipes in the programming language "Phyton" are part of Plattenbau. The desired material compositions were imported into "Plattenbau" by a text file. Subsequently, the software calculated all needed volumes of the reactants required by the parameterized sol–gel recipes and created a pipetting list, which was transferred to the pipetting robot.

The syntheses were carried out with the help of a commercial pipetting robot (Lissy, Zinsser Analytic). In the beginning, precursor solutions in 5 mL or 10 mL glass vials were placed on the desktop of the robot. By use of a pipetting needle the reactants were transferred to 2 mL vials (typical HPLC vials) arranged in racks of 50 vials.

The mixed metal oxides were synthesized by the ethylene glycol route [16], which was favoured for Ce, Co, Cr, and Ni based oxides. In this route mainly nitrates were used as precursors, which were dissolved in mixtures of ethylene glycol and water (100/54, v/v). Typically, 350 μmol of each material was prepared in the HT syntheses. The molar ratio of metal(s):ethylene glycol:H$_2$O:HNO$_3$(conc.) was 1:18:37.5:4. For example, Ce$_{10}$Ni$_{10}$Co$_{80}$O$_x$ was synthesized by pipetting 477 μL 0.587 M Co(NO$_3$)$_2$ solution, 60 μL 0.587 M Ce(NO$_3$)$_3$ solution and 60 μL 0.587 M Ni(NO$_3$)$_2$ into a 2 mL vial. Subsequently 84 μL of conc. HNO$_3$ was added to reaction mixture. After finishing all pipetting steps the 50 vessels rack was placed on an orbital shaker (Titramax 100, Heidolph) for the 1 h. The thermal treating was carried out under static air for 12 h at 80 °C (heating rate 20 °C/h), followed by 60 h at 105 °C (heating rate 20 °C/h). Finally, the sample was calcined for 5 h at 400 °C (heating rate 6 °C/h). The catalyst powders obtained were ground in flasks and transferred manually into 206 hexagonally positioned wells of a slate library. Two commercial hopcalite catalysts were used as reference materials.

The materials prepared were mixed-metal oxides of unknown oxidation states. Since oxidation states may vary with pretreatment, under reaction conditions and during catalytic oxidation reactions, oxidation states are not specified. The materials' compositions are identified by the mol% of metal ions as subscript. For instance Co$_{60}$Ni$_{40}$O$_x$ describes an oxide composed of 60 mol% Co and 40 mol% Ni oxides.

2.1.2. EcIRT

Our ecIRT setup for the testing of 206 catalyst samples in parallel as well as the measurement principles have been reported previously [13,17]. For this study the setup was enhanced by one additional mass flow controller for the dosing of the corrosive MeBr. The catalyst library was placed in the gas phase reactor, which has a semi-circular gas inlet and on the opposite side a semi circular gas outlet, and subsequently it was closed tightly with an IR transparent sapphire window on the top. For *in situ* observation of temperature changes on the surfaces of the catalyst bed the library was monitored by an IR camera of type PtSi 640 (Thermosensorik). The experimental procedure, including temperature regulation, gas dosing and camera setting, was managed by the in-house software IR-TestRig. The pre-treatment of the catalyst libraries was done in synthetic air at 350 °C for 1 h. For the six point temperature calibration the gas atmosphere was changed to $O_2:N_2 = 1:9$, the calibration itself was carried out in a ΔT range of $-4\,°C$ to $+6\,°C$ around the reaction temperature. Before start of the reaction, two IR images were taken under the calibration atmosphere. Then the gas mixture was changed to $CO:O_2:N_2 = 3:10:87$ for CO oxidation, $MeBr:CO:O_2:N_2 = 0.5:3:10:87$ for quenching of the CO oxidation by MeBr and benzene:$O_2:N_2 = 1:10:90$ for deep oxidation of benzene. During the reactions IR images were recorded after 1 min, 5 min, 10 min, 15 min, 30 min and 60 min time on stream. After reaction the reactor was flushed with calibration gas for 30 min and one additional IR image was taken to check for emissivity changes of the materials potentially resulting from the MeBr exposure.

2.2. Conventional testing

2.2.1. Conventional syntheses

The catalyst samples for conventional testing were prepared by the same ethylene glycol route as for the HT syntheses, only the scale was increased by a factor of 35 up to 12 mmol.

For example the $Ce_5Ni_5Co_{90}O_x$ catalyst was synthesized by adding to 18.4 mL 0.59 M $Co(NO_3)_2$ solution in a 50 mL beaker 1.02 mL 0.59 M $Ce(NO_3)_3$ and 1.02 mL 0.59 M $Ni(NO_3)_2$ solution under stirring. Then 3.34 mL conc. HNO_3 was pipetted to the reaction mixture. After additional stirring for 1 h the reaction mixture was splitted into three 20 mL glass vials. The thermal treating was done the same way as in the HT syntheses.

2.2.2. Conventional catalytic testing

The conventional catalytic testing was carried out in a plug-flow fixed bed reactor at atmospheric pressure. For the test 100 mg catalyst powder (of sieve fraction 100–200 μm) was diluted with 100 mg quartz sand (100–200 μm). The pre-treatment was done in synthetic air for 1 h with a flow rate of 50 mL/min. The composition of the feed gas mixture was $MeBr:benzene:CO:O_2:N_2 = 0.5:0.5:2:10:87$ at a WHSV 30 L/(g h). The gases were analysed offline by gas chromatography.

Product gas samples were taken by collecting the exhaust gas for 10 min in a gas tight bag. The bag was then transferred to the gas chromatograph Agilent GC6890 and analysed. The sample was first suctioned through the sample loop of the GC by a membrane pump for 1 min to flush the system. Then the separation of the gas mixture was carried out with three different columns on two measurement channels. One channel was equipped with "Gas Pro" column ($l = 30$ m, $d = 0.32$ cm) and a FID detector for hydrocarbons. The gases CO, CO_2, O_2 and N_2 were determined by a WLD detector. For the separation a "Plot-Q" column ($l = 10$ m, $d = 0.32$ cm) and a "Molsieb A5" column ($l = 10$ m, $d = 0.32$ cm) were used. All conversions were calculated in relation to the bypass gas composition.

Table 1
Model exhaust gas of terephthalic acid production [2].

Ingredient	Concentration	Ingredient	Concentration
Toluene	2 ppm	Methyl acetate	408 ppm
Benzene	2 ppm	Carbon monoxide	3500 ppm
p-Xylene	7 ppm	Water	4300 ppm
Methyl bromide	35 ppm	Oxygen	2.5–5%
Methanol	90 ppm		

2.2.3. Catalyst characterization

Nitrogen physisorption measurements were performed on a Carlo Erba Sorptomatic 1990 at $T = -196\,°C$. The samples were evacuated for 2 h at 200 °C with a heating rate of 5 °C/h. X-ray fluorescence spectroscopy data for elemental analyses were accumulated by an EAGLE μ-Probe II (Roenalytic). To quantify the elements the fundamental parameter model was used. Deionized water from a Drechsel bottle connected to the exhaust line of the plug flow reactor was analysed after gas phase reactions for catalyst elements to estimate catalyst leaching by ICP-MS on a VG Elemental Plasma Quad 3 Instrument (qualitative thus standard-less analyses).

3. Results and discussion

3.1. Development strategy

The combination of high throughput methods and combinatorial chemistry has sped up the research and development of new materials [10]. By enhancing the search space for new materials, chances for successful discoveries increase with the number of experiments. The careful design of experiments (DoE) at the beginning of a project determines whether the project has potential for new discoveries or whether only improvements of known materials can be achieved. An often used strategy is the combination of knowledge, random and systematic variation [11]. We have decided to begin this study with broad pre-screening experiments and a literature study, followed by a more rigid DoE. To start the pre-screening the model gas mixture and the temperature range of interest had to be defined. In parallel the literature was searched for melting points and sublimation points of volatile metal halides.

3.2. Definition of the parameter setup

The development started with the definition of the model gas mixture. In industrial processes the exhaust consists of a complex composition of different gas molecules. Lee et al. reported a model gas mixture for the off-gas of a terephthalic acid production line [2]. The ingredients and their concentrations are summarized in Table 1. MeBr formed by the aging of the $CoBr_2/MnBr_2$ catalyst during the terephthalic acid synthesis [18] is the compound with the major impact on the catalytic oxidation. The oxidation of the alkyl bromide itself produces HBr and Br_2 due to the Deacon equilibrium, which cause corrosion problems in and around the reactor. We have decided to simplify the model gas to CO and MeBr in synthetic air as most reactive ingredients and benzene was selected as the least reactive representative from the different hydrocarbons listed.

3.3. Influence of MeBr in pre-screening experiments

In previous projects broad screenings for CO oxidation catalysts have been carried out [12,19]. Some of the best catalysts from these projects have been used for pre-screening here. Most important to us was the effect of MeBr on the catalytic activity of these catalysts. Therefore the influence of MeBr on the CO oxidation was

Table 2

Comparison of the CO oxidation ecIRT results for the ten best catalysts out of 20 with and without presence of MeBr (feed gas compositions and flow: $CO:O_2:N_2 = 3:10:87$ (50 mL/min), $MeBr:CO:O_2:N_2 = 1:3:10:86$ (flow 50 mL/min) after 60 min on stream.

Material	Without MeBr		With MeBr
	Ranking	ΔT [°C]	ΔT [°C]
Hopcalite A	1	5.0	6.6
$Cr_{33}Cu_{33}Mn_{33}O_x$	2	3.5*	1.4
$Ce_5Co_{95}O_x$	3	2.8*	No exo. signal
$Ce_{10}Mn_{90}O_x$	4	2.0	2.7
$Pt_{0.5}Al_1Mn_{6.7}Co_{91.8}O_x$	5	1.9	0.2
$Cu_{20}Co_{70}Ni_{10}O_x$	6	1.6	2.8
$Co_{40}Ni_{60}O_x$	7	1.5	0.9
$Ce_{10}Co_{90}O_x$	8	1.4*	No exo. signal
Hopcalite B	9	1.3	0.3
$Ce_{10}Co_{80}Ni_{10}O_x$	10	1.0	1.2

Oxides marked with asterisk only one sample on the library is considered.

Table 3

Melting points of selected metal bromides from Gmelin database [20].

Transition metal bromide	Melting point [°C]
$CeBr_3$	783
$CoBr_2$	678
$CrBr_2$	812
$CrBr_3$	842
$CuBr$	490
$CuBr_2$	498
$FeBr_2$	684
$FeBr_3$	Decomp. to $FeBr_2$
$MnBr_2$	695
$NiBr_2$	963
VBr_2	Not stable
VBr_3	800 (sublimation)
VBr_4	Not stable

checked with 20 different, carefully selected CO oxidation catalysts. The binary and ternary mixed metal oxide catalysts mainly contain Ce, Co, Cr, Cu, Mn and Ni. Also one noble metal containing catalyst $Pt_{0.5}Al_1Mn_{6.7}Co_{91.8}O_x$ was tested. As references for the experiments two commercial hopcalites A (from Dräger Safety) and B (from Heraeus) have been placed on the slate library.

First the catalytic activity was checked without MeBr at 250 °C. After this test 0.5 vol% MeBr was added to the gas feed, the other experimental conditions were kept constant.

In Table 2 the results of the best catalysts without and with presence of MeBr are summarized. Listed are the area-averaged temperature increases (ΔT) as indicators of relative heats of reaction. The ΔT values were derived by taking the difference of the integration of the heat recorded for each catalyst well before and during the reaction. The Cu and Mn containing catalysts confirmed their known high catalytic activity for the CO oxidation reaction. An additional six Co based materials were under the top 10, specifically $Ce_5Co_{95}O_x$ and $Co_{40}Ni_{60}O_x$ with temperature increases of 2.8 °C and 1.5 °C. In addition, many of these Co based mixed oxides were doped with Ni.

The emissivity of catalyst powders often decreases in the presence of MeBr resulting in negative temperature changes. For example for the materials $Ce_5Co_{95}O_x$ and $Ce_{10}Co_{95}O_x$ the ecIRT images (see Fig. 1) show a complete loss of heat emission. In contrast to these oxides, $Ce_{10}Co_{80}Ni_{10}O_x$ reveals a nearly consistent ΔT without and with presence of MeBr of 1.0 and 1.2 °C. Ni might be important to stabilize the catalytic activity. This is confirmed by the material $Co_{70}Cu_{20}Ni_{10}O_x$ with a higher ΔT value in the presence of MeBr. Ce is necessary to promote the catalytic properties. This shows the comparison of $Co_{40}Ni_{60}O_x$ with $Ce_{10}Ni_{10}Co_{80}O_x$ mixed metal oxides.

The repetition of the ecIRT experiment with MeBr at 200 °C showed no remarkable changes in the catalyst ranking. Slight decreases of the heats of reaction were observed indicative of some degree of deactivation.

3.4. Literature data

The application of hopcalite in an industrial exhaust that contains MeBr is a big challenge due to the formation of $CuBr/CuBr_2$ and $MnBr_2$. Thus catalyst leaching is the main problem in this field. One reason for the catalyst discharge are the high reaction temperatures close to 400 °C, i.e. close to the melting points of metal bromides, for instance of CuBr with mp = 490 °C which results in an increase of the vapour pressure of the halides.

During this study two objectives came into the focus: (1) selection of catalyst elements whose bromides have significantly higher melting points than the reaction temperature and (2) the decrease

of the reaction temperature. In Table 3 the melting points of the most interesting element bromides for oxidation reactions are summarized. There is a remarkable a gap of nearly 200 °C between copper bromides and other metal bromides.

3.5. Catalyst development

Based on the melting point data and the ecIRT results from pre-screening the development strategy focused on the elements Ce, Cr, Co and Ni with the objective of replacing hopcalite as standard catalyst. These four elements were combined to four ternary metal oxide composition spreads Ce–Cr–Co, Cr–Co–Ni, Ce–Cr–Ni and Ce–Co–Ni. The contents of the elements were varied in the range between 10 and 80 mol% in 10 mol% steps. These composition spreads included no binary or pure metal oxides. Each oxide was placed three times on the materials library allowing averaging over the library plate position.

3.6. Ternary metal oxide composition spreads of Ce–Co–(Cr, Ni)

3.6.1. Ce–Co–Cr

A large number of the materials in the composition spread Ce, Co and Cr, especially with a Ce content of 30–80 mol%, showed no changes in temperature during the reaction. These materials should not be catalytically active. Nevertheless, the best material $Ce_{20}Co_{40}Cr_{40}O_x$ of the composition spread with $\Delta T = 0.4$ °C at 250 °C oxidizes in conventional plug flow experiments 59% CO and 12% benzene, but no MeBr at the same temperature as in the ecIRT experiments. The low ΔT value of this catalyst in contrast to high CO conversion is reasoned by an emissivity change of the material during the reaction. Such an emissivity change is mainly initiated by the formation of metal halides and/or the modification of the oxidation states. In consequence of no noticeable MeBr conversion the halide formation can be neglected in this case. Further the variation between Ce^{3+} and Ce^{4+} in O_2-rich atmosphere should have a significant influence on the material emissivity. Similar observations are reported by Loskyll et al. with iron oxides [14].

3.6.2. Ce–Cr–Ni

Materials in the range of Cr content between 20 and 50 mol% revealed high ΔT values over 1 °C. The best potential catalysts were Ce rich with 50–70 mol% Ce. Additionally, the materials have been tested for the decomposition of benzene as a low reactivity model compound for volatile hydrocarbons. The quantitative composition activity relationship (QCAR) diagrams (Fig. 2) for both experiments agree in one point: the mixed metal oxides $Ce_{70}Cr_{20}Ni_{10}O_x$ and $Ce_{50}Cr_{30}Ni_{20}O_x$ should have the highest catalytic activity.

The conventional plug flow experiment of the oxide $Ce_{50}Cr_{30}Ni_{20}O_x$ did not confirm the high heat of reaction from the
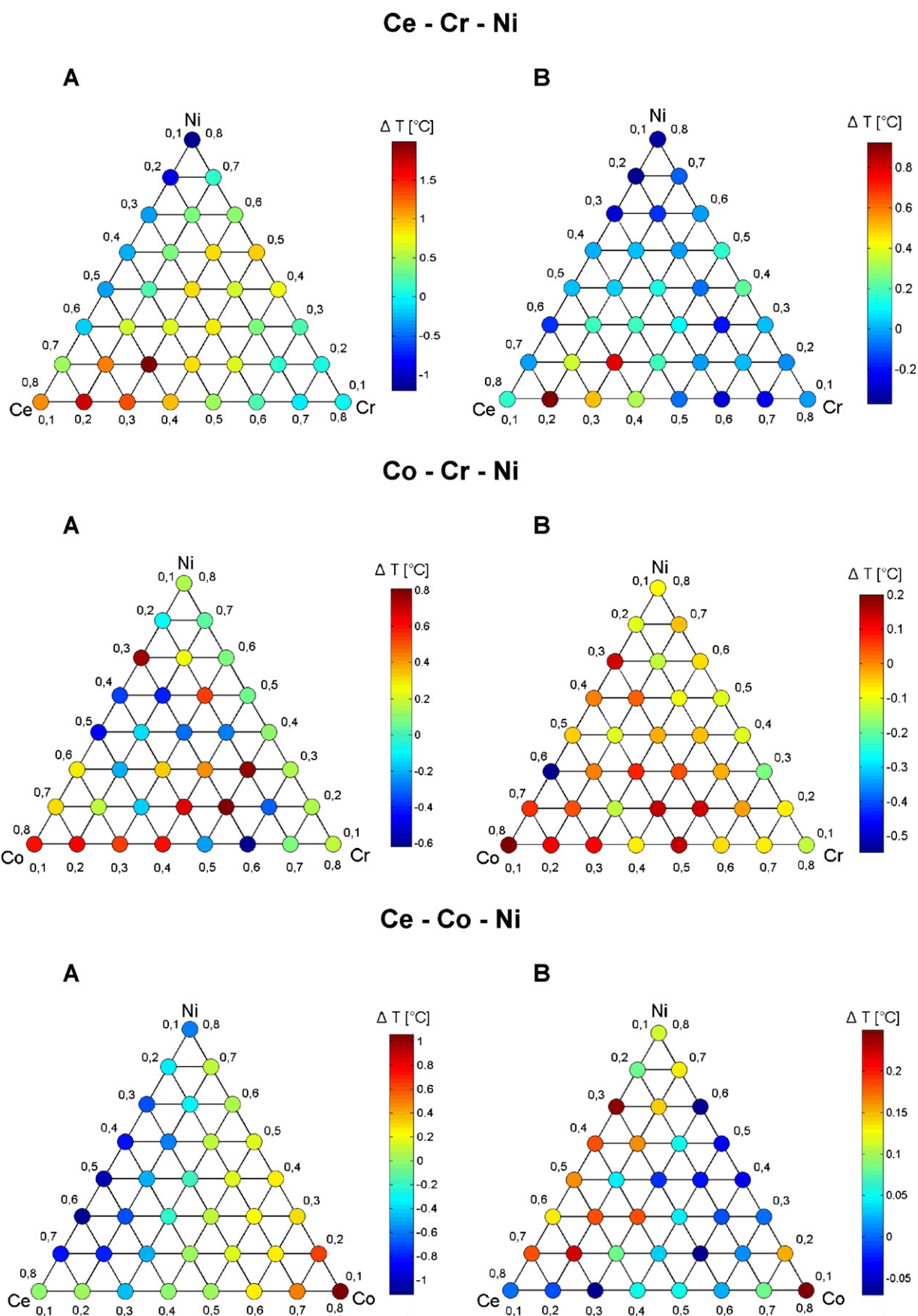
Fig. 2. QCAR diagrams for various ternary metal oxide composition spread libraries. (A) CO oxidation in the presence of MeBr; exp. conditions: $T = 250\,°C$, gas flow 50 mL/min, feed gas composition $MeBr:CO:O_2:N_2 = 0.5:3:10:86.5$. (B) Deep oxidation of benzene; exp. conditions: $T = 250\,°C$, gas flow 50 mL/min, feed gas composition benzene:$O_2:N_2 = 1:10:89$.

Table 4
Ranking of the best materials in the ternary metal oxide composition spread Co–Cr–Ni for the oxidation of CO and benzene.

Material	Ranking CO	ΔT_{CO} [°C]	Ranking benzene	$\Delta T_{benzene}$ [°C]
$Co_{30}Cr_{10}Ni_{60}O_x$	1	0.81	4	0.14
$Co_{30}Cr_{50}Ni_{20}O_x$	2	0.80	5	0.13
$Co_{20}Cr_{50}Ni_{30}O_x$	3	0.78	No exo. signal	0.00
$Co_{40}Cr_{40}Ni_{20}O_x$	4	0.66	2	0.15
$Co_{80}Cr_{10}Ni_{10}O_x$	5	0.60	1	0.20

ecIRT. At 300 °C the catalyst reaches only 40% CO conversion and the conversion of the VOCs remained below 20%.

3.6.3. Co–Cr–Ni

The composition spread of Co, Cr and Ni contained some catalysts with appreciable conversions, for example the Co rich oxides with 60–80 mol% Co. More active catalysts were found in the composition range of c(Co) = 20–40 mol%, c(Cr) = 30–50 mol% and c(Ni) = 20–30 mol%. The catalyst $Co_{30}Cr_{10}Ni_{60}O_x$, was a highly active catalytic material for MeBr oxidation. This is remarkable, because in its direct neighbourhood it was the only active one. Furthermore, the oxide was one of the most active five for the decomposition of benzene (see Table 4). For this reaction the Co richest composition $Co_{80}Cr_{10}Ni_{10}O_x$ was the best catalyst. Generally the comparison of the catalytically active areas in the QCAR diagrams (see Fig. 2) for the CO oxidation in the presence of MeBr and for the deep oxidation of benzene matched over a wide range. Even Co poor materials such as $Co_{20}Cr_{50}Ni_{30}O_x$ did not convert benzene in a sufficient manner.

The conventional validation of the catalyst $Co_{30}Cr_{10}Ni_{60}O_x$ confirmed the ecIRT results. At 300 °C the mixed metal oxide reached nearly full conversion of CO, benzene and MeBr. The reduction of the temperature to 250 °C led to a decline of the CO conversion to 80%. The other conversions of benzene and MeBr at this temperature were 30% and 20%, respectively. One potential problem with these materials is the possible formation of toxic Cr^{6+} species [7,21].

3.6.4. Ce–Co–Ni

The QCAR diagram for the CO oxidation in the presence of MeBr (Fig. 2) shows that with increasing Co content the exothermicity of the overall reaction increases. The highest ΔT value resulted for the composition $Ce_{10}Co_{80}Ni_{10}O_x$. This one also possessed a high ΔT value for the deep oxidation of hydrocarbons. In contrast to the CO oxidation in the presence of MeBr, Co poor oxides are also catalytically active for the oxidation of benzene, especially in the range of c(Ce) = 20–70 mol%, c(Co) = 10–20 mol% and c(Ni) = 30–70 mol%.

At low temperatures (250 °C) all the catalysts reached only full conversion for the CO oxidation, the decomposition of the VOCs approached 30% for benzene and 15% for MeBr determined by experiments in the plug flow reactor (Fig. 3). These conversion rates are as good as those of the hopcalite B (note hopcalite B is supported on alumina). An increase of the temperature tripled the conversion of the volatile molecules. Compared to the composition $Co_{30}Cr_{10}Ni_{60}O_x$ the composition $Ce_{10}Co_{80}Ni_{10}O_x$ was more promising for further optimization in so far as it does not contain elements known for the formation of volatile bromides.

3.7. Optimization

It is remarkable that with both characterization methods, ecIRT as well as plug flow reactor measurements, mixed metal oxides containing Co and Ni belong to the best catalysts. Therefore, a highly diverse doping of oxides with composition $E_xCo_{80-x}Ni_{10}$ with $x = 2$ or 10 mol% and various elements E was selected as a promising way to find the best elemental compositions for the total oxidation of the selected exhaust gas. Noble metals, most of the toxic elements
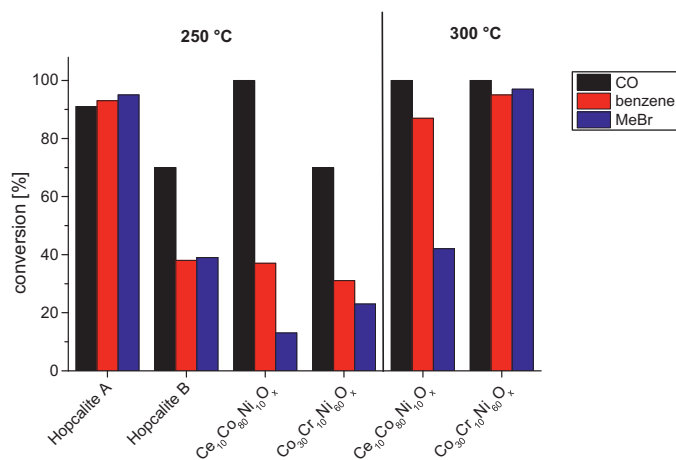

Fig. 3. Comparison of the mixed metal oxides $Ce_{10}Co_{80}Ni_{10}O_x$ and $Co_{30}Cr_{10}Ni_{60}O_x$ for the oxidation of VOCs and CO at the temperatures of 250 °C and 300 °C.

as well as the metals Cu and Mn have been explicitly excluded in this search. To optimize the elemental compositions 72 different materials were screened. An overview of the used elements is given in Fig. 4.

The screening of the library with the doped Co–Ni oxides was performed in analogy to the method used to test the four composition spreads mentioned above. From the experiments two groups of elements were identified, which enhance the catalytic activity for the oxidation of CO in the presence of MeBr and for the deep oxidation of benzene. The first group are including rare earth elements (RE), especially La and Pr, the second group the alkaline earth metals Ca, Sr and Ba. The amount of dopant does not affect the conversions significantly. These results correlate with reports of Weckhuysen and Van der Avert, who reported that basic metal oxides such as MgO, CaO, SrO, BaO and La_2O_3, CeO_2, Pr_2O_3, Nd_2O_3 favour for the decomposition of alkyl halides [22].

Due to these results, the catalyst development for pollutant oxidation in exhaust gases was focused on the optimization within the compositional ternary metal oxide field RE–Co–Ni. The Co content was varied between 78 and 90 mol% in 2 mol% steps, while the contents of La and Ni in the mixed oxides were varied from 2 to 20 mol%. The results are visualized in QCAR diagrams (see Fig. 5). The composition of the catalytically active materials confirms the observed trends resulting from the ecIRT tests. With increasing Co content the efficiency of the CO oxidation increases. The highest ΔT values (1.1 °C) are observed for the oxides $La_4Co_{90}Ni_6O_x$ and $La_6Co_{90}Ni_4O_x$.

Low overall ΔT values around 0.1 °C of the composition spread compared to the experiment errors (Fig. 5B) complicate the selection of the best material for the deep oxidation of benzene. In conventional experiments the conversions of benzene for the oxides $La_5Co_{90}Ni_5O_x$ and $La_8Co_{84}Ni_8O_x$ are close together (90% and 93% at 290 °C). It should be noted, that these experimental results are affected by similar changes of the emissivity as discussed for the Ce–Co–Cr composition spreads.

At this point the catalyst search was stopped with the compositions $RE_5Co_{90}Ni_5O_x$ (RE = La, Ce, Pr and Sm) as the best catalysts found. In further conventional plug flow experiments the influences of the rare earth elements on the catalytic properties have been studied.

3.8. Influence of rare earth elements as dopants

To study the catalytic activity of the four catalysts in the temperature range of 200–350 °C a model gas containing all components

Fig. 4. The doping elements used are shown with grey background.

in concentrations of 0.5 vol% MeBr, 0.5 vol% benzene, 2 vol% CO and 10 vol% O_2 balanced with N_2 has been selected.

All four rare earth doped Ni–Co catalysts expose full conversion of CO in the tested temperature range. The mixed metal oxides differ only in the light-off curves for the volatile hydrocarbons, especially for MeBr.

Fig. 6A and B shows the light-off curves for benzene and MeBr, respectively. For deep oxidation of benzene the three oxides doped with La, Ce and Pr show a similar catalytic performance with the exception of $Sm_5Ni_5Co_{90}O_x$, which exhibits a slightly higher light-off temperature. At 290 °C the Ce containing mixed metal oxide obtains full conversion of the aromatic compound.

The oxidation of MeBr starts at a temperature of 230 °C. Increasing the temperature induces a significant increase of the MeBr conversion for the oxide $Ce_5Ni_5Co_{90}O_x$. At 290 °C this catalyst is nearly twice as active as the La and Sm doped catalysts. As already seen for the deep oxidation of benzene, the Sm–Ni–Co oxide shows the lowest catalytic activity. It does not completely decompose the halogenated hydrocarbon in the temperature range investigated.

At this point, the temperature where 50% conversion was obtained (T_{50}) has been selected as characteristic indicator of catalytic activity. The lower T_{50}, the better is the catalyst performance. Our best catalyst obtains T_{50} values of 250 °C for the deep oxidation of benzene and 275 °C for decomposition of MeBr. In case of the benzene oxidation, the T_{50} value of $Ce_5Ni_5Co_{90}O_x$ is more than 50 °C lower than those of the perovskite structure type catalysts $LaCoO_3$ ($T_{50} = 323$ °C) and $LaMnO_3$ ($T_{50} = 301$ °C). For the pervoskite

Table 5

Comparison of performance of composition $Ce_5Co_{90}Ni_5O_x$ with different catalysts for the decomposition of halogenated hydrocarbons from literature.

Catalyst	T_{50} value	Halogen compound	Reference
$Ce_5Co_{90}Ni_5O_x$	274 °C	CH_3Br	This work
Cr/Al_2O_3	370 °C	CCl_4	[7]
$LaCoO_3$	351 °C	CH_2Cl_2	[25]
La/Al_2O_3	300 °C	CCl_4	[26]

catalysts the sample amount was 100 mg, benzene/O_2 1/100 and the space velocity 14,100 h^{-1} [23]. The comparison of the T_{50} values of MeBr decomposition is more difficult, since many publications have used chlorine containing compounds instead of MeBr. Furthermore, a comparison is complicated by the effect that increasing the Cl to C ratio leads to a decrease of the degradation temperature [24]. Nevertheless in Table 5 our newly developed catalyst compares well with some noble metal free catalysts from the literature.

Surface area and pore size distribution belong to the potentially important properties of heterogeneous catalysts. For all four catalysts both were determined to compare them to undoped cobalt oxide as reference material. The undoped cobalt oxide was prepared by the same recipe as the doped mixed oxides. In Table 6 the results of the BET surface determination for the four doped amorphous (determined by XRD) mesoporous mixed metal oxides and the undoped Co oxide are summarized. According to these measurements the observed catalytic activity is directly related to
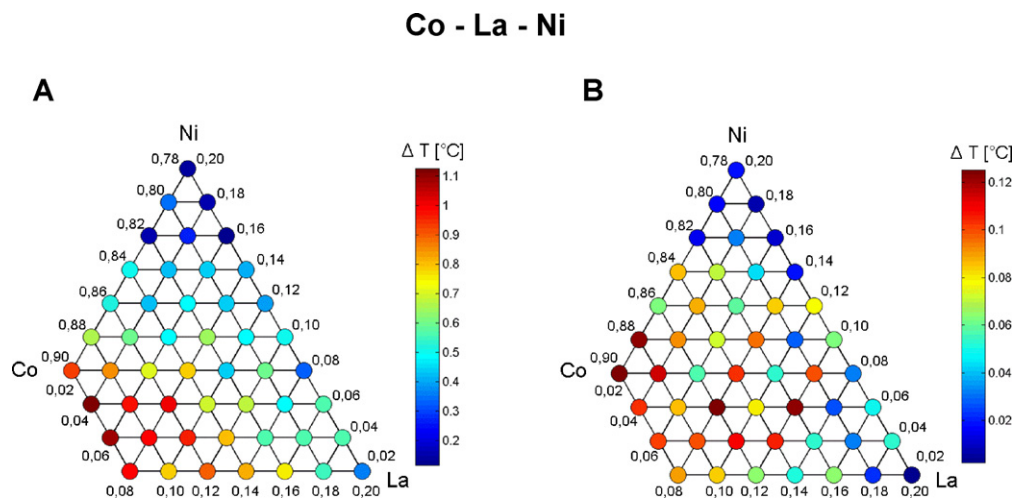

Fig. 5. QCAR diagrams for the ternary metal oxide composition spread Co–La–Ni. (A) CO oxidation activity in dependence of chemical composition of the catalysts in the presence of MeBr; exp. conditions: $T = 250$ °C, gas flow 50 mL/min, feed gas composition MeBr:CO:O_2:N_2 = 0.5:3:10:86.5. (B) Deep oxidation of benzene; exp. conditions: $T = 250$ °C, gas flow 50 mL/min, feed gas composition benzene:O_2:N_2 = 1:10:89.
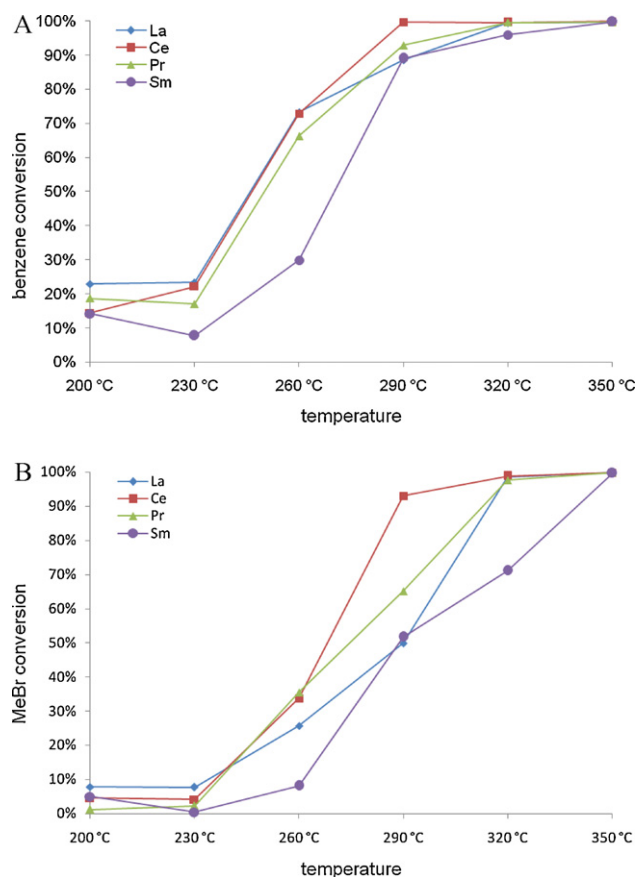
Fig. 7. Pore size distribution of undoped $Co_{100}O_x$ determined by BJH method.

Fig. 6. Light-off curves of the compositions $RE_5Co_{90}Ni_5O_x$ with RE: La, Ce, Pr and Sm. (A) For benzene oxidation and (B) for MeBr decomposition; exp. conditions: gas flow 50 mL/min, model gas composition MeBr:benzene:CO:O_2:N_2 = 0.5:0.5:2:10:87.

indicates, that these new catalysts interact more effectively with the hydrocarbon. The Sm-doped catalyst is less active, but most selective towards benzene decomposition. Since in all cases, as mentioned above, CO conversion on all these catalysts is quantitative, it has not been added to the table. The data in Table 7 also show, that our simplified use of catalytic activity throughout the manuscript is justified in this study, which is a search for alternative catalysts rather than a mechanistic study.

3.9. Long term study of $Ce_5Co_{90}Ni_5O_x$

Apart from a high conversion rate an excellent catalyst for the oxidation of CO and MeBr needs high long term stability. For that reason a laboratory scale plug flow experiment over 50 h on stream at 300 °C was performed. The model gas consisted of 1 vol% MeBr, 2 vol% CO and 10 vol% O_2 balanced with N_2. This large amount of MeBr compared to real industrial exhaust should stress the catalyst and should result in an accelerated aging.

Over the length of the experiment a full conversion of CO is observed. Furthermore no indication for negative impact of MeBr on the CO oxidation is found. The decomposition rate of MeBr fluctuates in range between 53 and 76% over time. In the end of the study 72% of the MeBr was destroyed.

Also of interest is the material composition before and after the long term tests. Table 8 shows the results of the XRF analyses. These results indicate no significant loss of any catalyst component during the long term study. The deviation of the Ni content from synthesis amount 5 mol% can be explained by the overlap of the $K\alpha$ line

the specific surface of the oxides. The material with the highest conversion of benzene and MeBr also had the highest surface area S_{BET} = 108 m²/g. In general the doping of Co oxide with Ni and RE elements results in a doubling of the BET surface. Furthermore, the doping also influences the pore size distribution determined by the BJH method. While Co oxide showed a broad monomial distribution with a main pore radius between 5 and 10 nm, the addition of 5 mol% Ce and 5 mol% Ni resulted in a narrowing of the pore size distribution with smaller radii in the range of 5 nm as shown in Figs. 7 and 8.

In Table 7 conversion rate was normalized to catalyst surface area loaded in the reactor. This normalization provides more reliable data on relative catalytic activity. Hopcalite A with the large surface area of 229 m²/g converts over 90% of the pollutants benzene and MeBr at 250 °C, which is double that of hopcalite B. In terms of conversion per surface area, however, hopcalite A is only 20% better than hopcalite B. For the rare earth doped Ni–Co oxides the tendency shown in Fig. 6A and B is confirmed. Ce, La and Pr doped catalysts convert more benzene/m² than the reference hopcalites. The significantly lower conversion of MeBr of all 3 materials

Table 6
BET surface and pore radius (pore radius determined by BJH method).

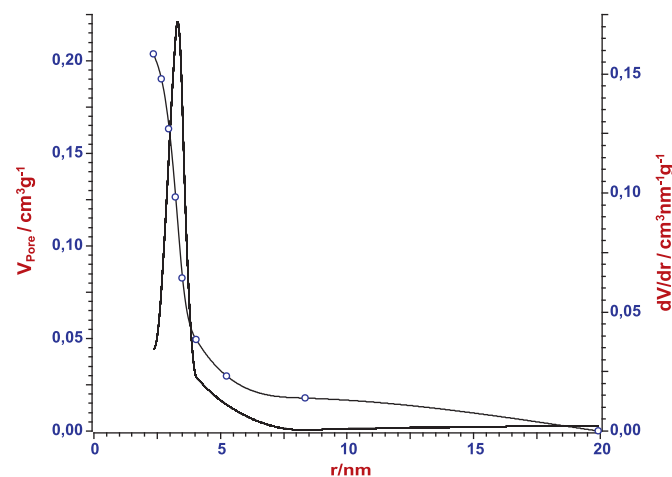| Oxide	S_{BET} [m²/g]	Maximum pore radius [nm]	Average pore radius [nm]
$Co_{100}O_x$	48	7.5	7.8
$Sm_5Co_{90}Ni_5O_x$	80	1.7	6.8
$Pr_5Co_{90}Ni_5O_x$	96	2.3	6.9
$La_5Co_{90}Ni_5O_x$	102	2.6	4.3
$Ce_5Co_{90}Ni_5O_x$	108	4.0	4.1

Fig. 8. Pore size distribution of $Ce_5Co_{90}Ni_5O_x$ determined by BJH method.

Table 7
Correlation between conversion of MeBr (benzene) and surface area of catalyst.

Catalyst	Temperature	Surface loaded in reactor	Surface hourly space velocity for MeBr/benzene	MeBr		Benzene	
		m^2	$L/(h\,m^2)$	Conversion X	X/m^2	Conversion X	X/m^2
$Ce_5Co_{90}Ni_5O_x$	260 °C	10.8	0.014	0.338	0.0313	0.728	0.067
$La_5Co_{90}Ni_5O_x$	260 °C	10.2	0.015	0.264	0.0259	0.715	0.070
$Pr_5Co_{90}Ni_5O_x$	260 °C	9.6	0.016	0.354	0.0369	0.662	0.069
$Sm_5Co_{90}Ni_5O_x$	260 °C	8.0	0.019	0.082	0.0103	0.299	0.037
Hopcalite A	250 °C	22.9	0.007	0.950	0.0415	0.930	0.041
Hopcalite B	250 °C	11.2	0.013	0.390	0.0348	0.380	0.034

Table 8
XRF catalyst composition analysis results of $Ce_5Co_{90}Ni_5O_x$ before and after long term catalytic test; exp. conditions for catalytic test: $T = 300$ °C, time on stream 50 h, gas flow 50 mL/min, model gas composition $MeBr:CO:O_2:N_2 = 1:2:10:87$.

Element	Before catalytic test		After catalytic test	
	wt%	mol%	wt%	mol%
Ce	9.3	4.1	7.9	3.5
Co	82.9	87.6	84.1	88.2
Ni	7.7	8.2	7.9	8.3

of Ni (7.477 eV) and the Kβ line of Co (7.640 eV). Additionally the Drechsel bottle water was probed by ICP-MS after bubbling the product gas through the Drechsel bottle for the entire measurement period of 50 h. Compared to a blank probe of deionized water, which was taken after bubbling the feed through the Drechsel bottle for 2 h without catalyst, also no Ce, Co or Ni ions were detected in the water probed after gas phase reaction with the $Ce_5Co_{90}Ni_5O_x$ catalyst. These results indicate that the catalyst is sufficiently stable under the reaction conditions chosen.

4. Conclusions

In this study high throughput technologies have been applied to screen for new catalysts as well as optimize the most promising materials for the purification of CO and MeBr containing exhaust gases. With the help of ecIRT as a screening tool and validation by conventional gas phase plug flow experiments the catalytic activity of 250 different materials under variable gas atmospheres and temperatures has been studied.

During the screening experiments three lead compositions have been identified, which may potentially substitute Cu–Mn based metal oxides as exhaust control catalysts:

1. $Ce_5Co_{90}Ni_5O_x$
2. $Co_{30}Cr_{10}Ni_{60}O_x$
3. $Ce_{20}Co_{40}Cr_{40}O_x$

Co is needed for a sufficient CO oxidation at 250 °C, since oxides in the composition spread studies without Co (Ce–Cr–Ni) showed only low CO conversion, while the Co-based materials gave complete CO conversion. ecIRT and conventional studies suggest that Ni doping reduces the poisoning of Co oxide by halide compounds and stabilizes their catalytic performance. Rare earth metals and alkaline earth metals are able to promote the catalytic activity for decomposition of pollutants in the presence of halogenated VOCs. The differences in the conversion of benzene and MeBr for the tested $RE_5Co_{90}Ni_5O_x$ (RE = Ce, La, Pr and Sm) catalysts showed a more effective conversion of benzene relative to the hopcalite reference catalysts. The differences in conversion could be attributed to differences in surface areas. The oxide $Ce_5Co_{90}Ni_5O_x$ is considered most promising for an industrial application, since the catalyst consists of metals, which form stable metal bromides under the chosen reaction conditions. That was confirmed in a 50 h long time experiment, where no decline in CO oxidation was observed in the presence of MeBr. Also the metal oxide composition was identical before and after the test.

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